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S. W. STRATTON, DIRECTOR

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CEMENTS FOR SPARK-PLUG ELECTRODES

BY

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Bureau of Standards

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By Homer F. Staley

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I. INTRODUCTION

Considerable trouble has been experienced in the operation of airplane engines, due to breaking of the central electrode wires in spark plugs at the point where it enters the porcelain. For this reason the Bureau of Aircraft Production, under date of August 19, 1918, requested the Bureau of Standards to investigate this problem.

Examination of numerous broken spark plugs showed that at the point of failure the central electrode wire was oxidized practically through its cross section. This oxidation extended up into the spark plug a variable distance, depending upon the permeability of the cement with which the wire was surrounded. In some cases the cement had melted and run down along the wire. It was apparent from the nature of the failures that, in order to study the problem thoroughly, the properties of the electrode wire, porcelain insulator, and the cement used to secure the wire to the insulator, must be investigated.

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II. PROPERTIES OF THE MATERIALS EMPLOYED

(*a*) ELECTRODE WIRES.—The material most commonly used for central electrodes in spark plugs is known as 97 per cent spark point nickel wire. In the particular type of plug which gave trouble, the entire central electrode was of this material. The following are typical analyses:

Composition of Wire

Laboratory No.		47134	47135
Nickel [a]	per cent	97.0	96.9
Manganese	do	1.5	1.6
Iron	do	.8	.9
Copper	do	.4	.2

[a] Contains cobalt, probably as much as 1 per cent. Some wires contain as much as 0.25 per cent silicon.

The thermal expansion of this wire as determined by the Bureau is given below:

Thermal Expansion of Wire

Temperature interval	Average coefficient
25 to 200 C	14 x 10^{-6}
200 to 400 C	16
400 to 600 C	16
600 to 840 C	20
25 to 840 C	17

(*b*) PORCELAIN.—For making porcelain insulators, one spark plug manufacturer uses a modification of Bureau of Standards body No. 152, the thermal expansion of which is as follows:

Thermal Expansion of Porcelain

Temperature interval	Average coefficient
30 to 200 C	3.36 x 10^{-6}
200 to 400 C	3.36
400 to 520 C	4.19
30 to 400 C	4.78
30 to 520 C	3.81
	4.06

This porcelain is of a special type developed by the ceramic division of the Bureau and will be described in a paper to be prepared by that division. In addition to low coefficient of expansion, it is remarkable for its comparatively great mechanical strength.

Another manufacturer uses porcelain having the following thermal expansion.

Temperature interval	Average coefficient
24 to 200 C	5.7 x 10^{-6}
200 to 400 C	6.7
400 to 540 C	8.4
24 to 540 C	6.8

(*c*) CEMENTS.—It developed through correspondence with various manufacturers that most of the cements used between wire and porcelain consisted of mixtures of silicate of soda with finely powdered solids, which were supposed to be chemically inert. Barium sulphate was the solid used by the manufacturer whose plugs gave the most trouble, while another maker, whose plugs are used in large quantities for airplane work, employed finely ground silica. Silicate-of-soda cements are advantageous for this work because they are cheap, can be worked cold, and are gas tight at low temperatures.

III. TESTS OF VARIOUS CEMENTS

To determine the effect of various cements on electrode wires, mixtures were made of silicate of soda and typical powdered materials. Small pellets of these mixtures were worked around commercial nickel electrode wires, and after drying at 120° C., the wires and adhering pellets were heated in an oxidizing atmosphere to 500° C and then to 1000° C. These temperatures probably limit the range of temperatures attained at the tip of the porcelain of a spark plug in an airplane engine in operation. After cooling, the pellets were broken off and the wire beneath them examined. The results for the heating to 1000° C are given in Table 1. In the heating to 500° C the effect of the various compositions was not so marked but the relative effects were substantially the same.

TABLE 1.—Effect of Cements on Electrode Wires

Cement No.	Sodium silicate 40° Baumé, cubic centimeters	Water, cubic centimeters	Solid		Effect of heating to 1000° C	
			Grams	Kind	Oxidation	Description
1	5	5	30	Powdered silica.....	Very bad.....	Hard, strong, slightly porous; part of material had run down the wire.
2	10	.....	30	.....do.....	.....do.....	Do.
3	5	2	30	Barium sulphate.....	Eaten through..	Part of material had melted and run down wire, leaving a hard blue mass behind.
4	7	.....	30	.....do.....	.....do.....	Do.
5	5	5	30	Kaolin.....	None.....	Hard, strong; very slightly porous.
6	10	.....	30	.....do.....	.....do.....	Hard, strong; not porous.
7	5	9	15 15	.....do..... Aluminum oxide.....	Very bad.....	Soft, weak, porous.
8	10	4	15 15	Kaolin..... Aluminum oxide.....	.....do.....	Do.

TABLE 1.—Effect of Cements on Electrode Wires—Continued

Cement No.	Sodium silicate 40° Baumé, cubic centimeters	Water, cubic centimeters	Solid		Effect of heating to 1000° C	
			Grams	Kind	Oxidation	Description
9	5	13	30	Aluminum oxide.....	Very bad.....	Soft, powdery mass.
10	10	8	30	.....do.....	.....do.....	Do.
11	10	8	30	Kaolin calcined at 500° C.	.....do.....	Hard, weak, porous.
12	10	16	30	Kaolin calcined at 750° C.	.....do.....	Do.
13	10	14	30	Kaolin calcined at 1000° C.	.....do.....	Soft, weak, porous.
14	10	12	30	Kaolin calcined at 1250° C.	.....do.....	Medium, hard weak, porous.
15[a]	.....	.....	.....	.....	.....do.....	
16[b]	.....	.....	.....	.....	Slight.....	

[a] Wire dipped in 40° Baumé sodium silicate. [b] Clean wire.

(*a*) SODIUM SILICATE AND POWDERED SILICA.—From Table 1, it appears that the solids used do not act simply as inert materials. Hydrated sodium silicate alone bakes at temperatures well below 500° C to sodium-silicate glass. The composition of this glass is approximately 25 per cent Na_2O and 75 per cent SiO_2. Its constitution, as that of all glasses, is unknown. It can be represented best by the formula $Na_2O\ x\ SiO_2$. Since sodium oxide is capable of forming glasses with widely varying amounts of silica, the reaction of sodium silicate with powdered silica consists of the solution of the finest particles of silica and the formation of a glass higher in silica than the original sodium-silicate composition. That the glass dissolved some oxide of nickel was shown by its bluish color. This glass must have been quite fluid, for the bulk of it ran down the wire, leaving behind a porous mass of silica grains coated and cemented together by thin films of glass.

(*b*) SODIUM SILICATE AND BARIUM SULPHATE.—Seger [1] has shown that molten sodium-silicate glass and barium sulphate react to form a glass consisting for the most part of barium silicate and glass gall made up largely of fused sodium sulphate. We may assume that this is what happened in cements Nos. 3 and 4. The formation of molten sodium sulphate accounts for the marked attack of this composition on the wire forming the electrode. The action of this mixture when heated readily explains the trouble arising in its use as cement for electrode wires in airplane engines.

[1] Collected Writings of Herman A. Seger, 2, p. 636, published by Chemical Publishing Co., Easton, Pa.

(*c*) SODIUM SILICATE AND ALUMINUM OXIDE.—A reaction took place in the cold between the sodium silicate and the precipitated aluminum oxide used in several of the cements as soon as they were blended. The resulting product was a rather friable, porous mass resembling plaster of Paris and entirely different from the hard vitreous-coated masses obtained when sodium silicate is mixed in the cold with inert substances such, for instance, as powdered silica. The action may have consisted of the formation of sodium aluminate or of sodium-aluminum silicate.

(*d*) SODIUM SILICATE AND CALCINED KAOLIN.—A similar action, but not so marked, seems to have taken place in the cold with calcined kaolin. When kaolins are calcined to temperatures between 450 and 1000° C they lose their two molecules of water and undergo a decrease in specific gravity; they also became much more active chemically in the cold than uncalcined kaolin.[2] This chemical activity is shown by the fact that calcined kaolin reacts with hydrated lime to form pozzuolanic cement and that it is much more soluble in acids than uncalcined kaolin.[3] When brought into contact with a strongly alkaline substance such as sodium silicate, calcined kaolin reacts quite rapidly to form a friable, porous mass.

As shown in the table, the porosity of the masses containing precipitated alumina and of those containing kaolin calcined at temperatures between 500 and 1000° C was retained on heating, the result being porous masses of little strength. The kaolin calcined at 1250° C had been rendered more nearly inert and when blended with sodium silicate gave products with properties midway between those of mixtures containing kaolin calcined at lower temperatures and of those made with the use of practically inert powdered silica.

(*e*) SODIUM SILICATE AND RAW KAOLIN.—Compositions made of mixtures of raw, or uncalcined, kaolin with sodium silicate were superior to others in that they did not fuse and were but slightly porous, thus protecting the electrode wires from oxidation. Raw kaolin is an extremely fine-grained substance which does not react in the cold with sodium silicate with the formation of a porous mass, as do precipitated alumina and calcined kaolin, but forms mixtures that dry to hard nonabsorbent masses. On heating such a composition water is driven off from both the sodium silicate and the kaolin and the remainder bakes to an impervious porcelain-like mass. The mechanism of this action is probably similar to that operating in the vitrification of a piece of porcelain, consisting of

[2] Knote, J. M., Trans. Am. Cer. Soc., 12, pp. 226–235.

[3] Knote, J. M., loc. cit. Bleininger, A. V., Manufacture of Hydraulic Cements, Geological Survey of Ohio, fourth series, Bull. 3, p. 25.

the formation of a viscous glass, the coating of the grains of unfused materials by this glass due to surface tension forces, the drawing together of the unfused particles by the same forces, and finally the congealing of the glass as the mixture is cooled.

No doubt complex chemical reactions are involved in the above process but we are no more able to write these reactions than we are those taking place in the formation of a piece of porcelain or a pot of molten glass. From the standpoint of utility as cement for spark plug electrodes, the important points are that there is no reaction in the cold and that the glassy portion of the mixture at no stage of the process becomes sufficiently fluid to flow away from the unfused portion, and thus yields a nonporous instead of a porous substance. This is unquestionably due to the gradual assimilation into the glass of a portion of the alumina and silica of the kaolin. It is well known that the addition of either of these substances to alkaline glasses tends to produce greater viscosity.

IV. RELATION OF THE USE OF CEMENTS TO THE FAILURE OF SPARK PLUGS FOR MECHANICAL REASONS

(*a*) Breakage of Porcelains.—The relation of the cement to the cracking of porcelains was clearly demonstrated on the occasion of a visit made by a representative of the Bureau to a spark-plug factory. In this plant porcelains were subjected to a sudden heating test, in which the tip of the porcelain was placed in the flame of a Meker burner. The porcelains were uniformly passing this test. When it was suggested that porcelains containing electrodes cemented in place be tested in the same manner, it was found that 45 per cent of the porcelains cracked. In the 55 per cent of plugs that did not fail, either cement was absent from around the wire near the tip of the porcelain or else it softened and gushed out of the hole. As the result of actual engine tests of complete plugs at the Bureau, it has been found in general that in the cracked plugs the cement is holding well and that plugs in which the porcelain is not cracked generally leak around the electrode wire. These failures are due in many cases, apparently, to the difference in coefficient of thermal expansion between the porcelain and nickel wire which sets up so high a stress between the two parts of the plug that either the porcelain or the cement has to give way.

(*b*) Attempts to Use Glass Seals.—Attempts were made to seal the wires into porcelains after heating by means of glasses, ranging in coefficient of thermal expansion from that of the

porcelain to that of the wire. None of these attempts was successful, for, in cooling, the glass pulled away either from the porcelain or from the wire and the spark plugs leaked badly. From a knowledge of the technique used in sealing metal into glass for various purposes, we know that it would be possible to use glass seals for electrode wires in at least two ways. One method would depend on having about the same coefficient of thermal expansion in porcelain, glass used for sealing, and electrode wire. Another would employ porcelain and glass of the same coefficient and seal this glass to metal electrodes or portions of electrodes of such thin cross section and consequent low mechanical strength that they would expand and contract with the glass. The use of either of these two methods of spark plug construction would involve various questions of heat conductivity, electrical resistance, kind of spark produced, etc., a discussion of which lies beyond the scope of this paper.

TABLE 2.—Gas Leakage Around Electrode Wires in Spark Plugs that Had Been Used for 1¾ Hours in a Liberty Engine

Condition of porcelain	Gas leakage	Loose electrode wires	Wires easily pulled out
12 broken [a]	6 bad	4	1
	6 none	None.	None.
28 not broken	17 bad	12	9
	8 moderate [b]	3	2
	3 none	None.	None.

[a] Part of these may have been broken while the plugs were being removed from the engines.
[b] More than 0.2 cm^3 per second.

(*c*) Gas Leakage.—The subject of gas leakage of spark plugs in relation to failure of the central electrode has also been studied. While considerable work has been done in determining the gas leakage of new plugs in view of the above results it appeared advisable to determine leakage on plugs that had been used in an airplane engine. In Table 2 are given the results of examination of a typical lot of 40 plugs. The leakage was measured by L. G. Sawyer, using the regular methods of the ignition staff of the Bureau. The following information will be of assistance in reading this table: Of the 12 broken plugs, 6 leaked badly and 6 did not leak at all; of those that leaked badly, 4 contained loose wires, and in the case of 1 of these the wire could be pulled out easily. It is evident that tests for gas leakage on new plugs give no indication of their gas leakage after use and that this leakage does not necessarily produce broken porcelains.

(*d*) Spark Plugs With Mechanical Seals.—On account of the difficulties incident to the use of cement between the electrode wires and porcelains in spark plugs, the elimination of the cement and the use of a mechanical seal at the top of the porcelain is greatly to be desired. The mechanical stress incident to the use of such seals should be localized at the top of the plug. The type of porcelain developed by the Bureau in body No. 152 has sufficient strength to withstand the necessary stresses. At least two manufacturers of spark plugs are following the above suggestion of the Bureau and tests of spark plugs made in this manner have shown that this type of construction gives good serviceable spark plugs and that it offers possibilities of successful commercial development. The mechanical seals can be made in a variety of ways. The Bureau is interested in suggesting the type of construction. In this connection it may be noted that spark plugs with glass insulators are made without the use of cement. In this case the glass is sealed directly onto thin wire electrodes.

V. SUMMARY

1. Of various typical cements for spark-plug electrodes made by mixing silicate of soda with different powdered solids, a mixture of raw kaolin with silicate of soda was found most satisfactory.

2. Chemical reactions take place either in the cold or on heating between silicate of soda and the solids commonly blended with it in making cements for spark-plug electrodes. With the exception of those occurring in blends of raw kaolin and silicate of soda, these reactions impair the utility of the mixtures for use as cements and promote the destruction of the electrode wires.

3. The practice of cementing electrode wires with high coefficient of thermal expansion into porcelains with low coefficients tends to produce cracked porcelains in spark plugs in use.

4. Gas leakage in moderate or large amounts was found in 90 per cent of a typical lot of used spark plugs in which the porcelain was not broken. It was evident that in these cases the cement failed instead of the porcelain and that gas leakage does not necessarily produce broken porcelains.

5. Preliminary tests indicate that it is possible to produce satisfactory spark plugs by the use of mechanical seals and thus to avoid the use of electrode cements with their attendant disadvantages.

Washington, August 22, 1919.